

Crystal Growth and Structure of a New PbHNSO₃ Crystal

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Abstract

A new type of PbHNSO₃ crystal has been grown by a gel method using agar-agar gel. TG-DTA and X-ray diffraction measurements have been performed on single crystal samples of PbHNSO₃. It is found that the thermal decomposition of the compound starts at about 960 K. The space group (orthorhombic *Pnma*) and structural parameters are determined at room temperature with unit cell dimensions: *a*=8.4690(6), *b*=5.3934(4) and *c*=6.9530(4) Å. The crystal structure is found to consist of NSO₃ pseudo-tetrahedra, PbO₉N₃ polyhedra, and NSO₃-Pb-NSO₃ frameworks. The dark brown color of the crystal is suggested to be caused by the absorption of blue wavelengths of light which is due to the excitation of excess electrons in potential wells produced by the NSO₃-Pb-NSO₃ framework.

Keywords: crystal growth, gel method, crystal structure, PbHNSO₃, TG-DTA, X-ray diffraction

1. Introduction

It is well known that crystals of an ANH₂SO₃-type consist of a monovalent cation ($A^+=Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, NH_4^+, C(NH_2)_3^+$ or $(CH_3)_3NCH_2COOH^+$) and a sulfamate $[NH_2SO_3]^-$ anion (Belaj et al., 1987; Cox et al., 1967; H. Haussühl & S. Haussühl, 1995; Manickkavachagam & Rajaram, 1984; Wadhawan & Padmanabhan, 1972). The crystal systems, space groups, lattice parameters, and elastic constants of the compounds at room temperature have been listed in the paper as reported by H. Haussühl and S. Haussühl (1995). It is confirmed from these data that three crystals containing larger cations, such as $A^+=Cs^+, C(NH_2)_3^+$ or $(CH_3)_3NCH_2COOH^+$, are of monoclinic system, and other crystals are of orthorhombic system. The KNH₂SO₃ and NaNH₂SO₃ crystals undergo phase transitions at 437.9 K with a transition enthalpy ΔH of 4.9 kJ/mol and at 456.0 K with ΔH of 1.9 kJ/mol, respectively (Budurov et al., 1997). Recently, it has been reported that the KNH₂SO₃ crystal also undergoes another phase transition at 350 K and becomes an ionic conductor at high temperature, and the CsNH₂SO₃ crystal has a structural phase transition from monoclinic *P2₁/c* to orthorhombic *Pnma* at 330 K (Varughese et al., 2010; Kumar et al., 2011; Fukami et al., 2011). The sulfamic acid and its derivatives are interested in industrial applications, and are widely used in a variety of applications such as a fireproofing agent, an anticorrosive agent, a cross-linking agent for polymers, and a cleaning agent for air, etc (Benson & Spillane, 1980). The NH₄NH₂SO₃ and C(NH₂)₃NH₂SO₃ compounds of the ANH₂SO₃-type have good abilities as fire retardant (Benson & Spillane, 1980).

The crystals of an A(NH₂SO₃)₂-type consist of a divalent cation ($A^{2+}=Ca^{2+}, Mn^{2+}$ or Ni^{2+}) and the sulfamate $[NH_2SO_3]^-$ anion (Angerer et al., 1999). The crystal structure of Ca(NH₂SO₃)₂·4H₂O is monoclinic with space group *C2/c*, and is built up of CaO₈ polyhedra and $[NH_2SO_3]^-$ anions. Four O atoms of the polyhedron are shared with four $[NH_2SO_3]^-$ anions around the Ca²⁺ cation. Similarly, the crystal structures of Mn(NH₂SO₃)₂·4H₂O and Ni(NH₂SO₃)₂·4H₂O are monoclinic with space group *P2₁/c* and triclinic with space group *P1̄*, and are built up of MnO₆ and NiO₄N₂ octahedra, respectively. Two atoms (O or N) of the octahedra in the two compounds are also shared with two $[NH_2SO_3]^-$ anions around the cations. Moreover, powder and single crystals of Pb₃(OH)₂(NH₂SO₃)₄ containing divalent Pb²⁺ cations are synthesized by a hydrothermal synthesis method using PbO and NH₂SO₃H as source materials (Wickleder, 2005). The crystal has an orthorhombic structure with space group *Pnma*, and consists of chains of OH⁻ centered $[Pb^{2+}]_3$ triangles and four types of PbO(N)_{*x*} (*x*=8-10) polyhedra (Wickleder, 2005). It is noticed that the chemical formula of the Pb₃(OH)₂(NH₂SO₃)₄ crystal differs from that of the A(NH₂SO₃)₂-type crystal in spite of that lead cation has a positive charge of +2*e*. Studies of physical and chemical properties of the compounds containing the divalent cation and the sulfamate anion are extremely rare.

The purpose of this paper is to synthesize the title compound containing Pb^{2+} and NSO_3^{3-} ions by using a gel method, and to determine the crystal structure at room temperature by X-ray diffraction.

2. Experimental

2.1 Crystal Growth

Single crystals of PbHNSO_3 were grown at room temperature by a slow diffusion method using agar-agar gel with U-shape tubes. The U-tubes with both ends open, arm length of 180 mm and diameter of 18 mm were used as crystallizing vessels. The agar-agar gels of concentration 1% were prepared by dissolving 2.0 g of agar-agar powder in 200 ml of distilled water at boiling temperature. After setting and aging the agar-agar gel (about 35 ml) filled up in the U-tubes, 10 ml aqueous solutions of $\text{Pb}(\text{NO}_3)_2$ (0.2 to 1.5 M) and of $\text{NH}_2\text{SO}_3\text{H}$ (0.2 to 2 M) were poured into each two limbs of a number of the tubes. The ions from the solutions diffused through the agar-agar gel, and prismatic shaped dark brown crystals with dimensions of typically less than $0.5 \times 0.5 \times 2.0$ mm were grown in the gels of all the tubes over several months.

2.2 Thermal Measurements (DSC and TG-DTA)

Differential scanning calorimetry (DSC) and thermogravimetric-differential thermal analysis (TG-DTA) measurements were carried out using DSC7020 and TG/DTA7300 systems from Seiko Instruments Inc, respectively. The amounts of the sample for the DSC and TG-DTA measurements varied between 2.63 and 7.68 mg. The heating rates for the DSC and TG-DTA measurements were 10 and 20 K/min with flowing dry N_2 gas at 40 and 200 ml/min, respectively.

Table 1. Crystal data, intensity collection and structure refinement for PbHNSO_3

Compound, M_r	PbHNSO_3 , 302.27
Crystal shape, color	Prism, dark brown
Temperature	297 K
Crystal system, space group	Orthorhombic, $Pnma$
Lattice constants	$a=8.4690(6)\text{\AA}$, $b=5.3934(4)\text{\AA}$ $c=6.9530(4)\text{\AA}$
V , Z	$317.59(4)\text{\AA}^3$, 4
$D(\text{cal.})$, $\mu(\text{Mo } K\alpha)$, $F(000)$	6.322Mg/m^3 , 53.59mm^{-1} , 520
Sample shape, size in diameter	Sphere, $2r=0.32\text{mm}$
θ range for data collection	$3.79\text{--}38.66^\circ$
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$
Reflections collected, unique	6500, 955 [$R(\text{int})=0.1191$]
Completeness to θ	97.8%
Absorption correction type	Spherical
Transmission factor $T_{\min}$ – $T_{\max}$	0.0013–0.0157
Data, parameter	687 [$I > 2\sigma(I)$], 35
Final R indices	$R_1=0.0418$, $wR_2=0.1243$
R indices (all data)	$R_1=0.0586$, $wR_2=0.1285$
Weighting scheme	$w=1/[\sigma^2(F_o^2) + (0.0340P)^2]$ $P=(F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	1.239
Extinction coefficient	$0.0(6) \times 10^{-3}$
Largest diff. peak and hole	5.257 and $-3.308\text{e}\text{\AA}^{-3}$

2.3 X-Ray Crystal Structure Determination

The X-ray diffraction measurements were carried out by using a Rigaku Saturn CCD X-ray diffractometer with graphite monochromated $\text{Mo } K_\alpha$ radiation ($\lambda=0.71073\text{ \AA}$). Diffraction data were collected at 297 K using an ω scan mode with a detector distance of 40 mm to the sample crystal, and processed using the CrystalClear software package. Intensity data were corrected for Lorentz polarization and absorption effects. The structure

was solved with direct methods of SIR2008 and refined on F^2 by full-matrix least-squares methods using SHELXL-97 program in the WinGX program package (Burla et al., 2007; Farrugia, 1999; Scheldrick, 1997). A summary of crystal data, intensity collection and structure refinement is given in Table 1. The highest peak and deepest hole of residual electron density in the final difference Fourier map were 5.257 and -3.308 $\text{e}\text{\AA}^{-3}$, and were located 0.84 and 0.67 $\text{\AA}$ from the Pb atom, respectively. The large values of the residual electron density are probably due to an effect associated with the presence of the heavy lead atom and to using wide-angle reflection data in the least-squares refinement.

3. Results and Discussion

3.1 Thermal Analysis

Figure 1 shows the TG, differential TG (DTG), and DTA thermal analysis curves at temperatures up to 1320 K. Broad and three small endothermic peaks in the DTA curve are observed at about 960, 1150, 1220, and 1240 K, respectively. The broad peak at 960 K corresponds to the temperature at which steep weight loss occurs in the TG curve and to a first peak in the DTG curve. The weight loss of about 4.6% is observed at around 960 K. It is also seen that the small exothermic peaks at 1150 and 1240 K in the DTA curve are nearly equal to start and end temperatures of a second weight loss in the TG curve. The weight loss of about 9.5% is observed in the temperature range of 1150-1240 K.

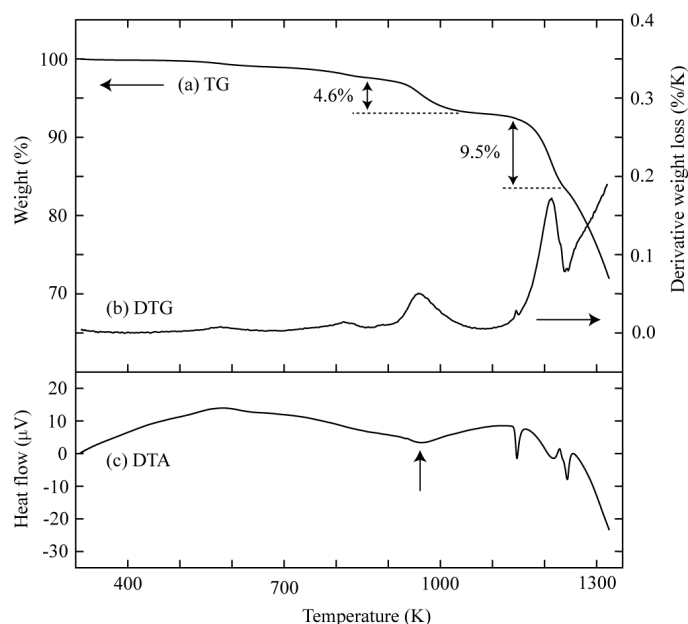


Figure 1. TG, DTG, and DTA thermograms of PbHNSO_3 on heating process. Sample weight was 6.031 mg, and the heating rate was 20 K/min under a dry nitrogen flux of 200 ml/min

The chemical formula of the sample crystal is represented as PbHNSO_3 with a molecular weight of 302.27 by the results of crystal structure determination, as described in the subsection on X-ray diffraction below. The theoretical weight loss at around 960 K, assuming the decomposition accompanied by the evolution of N_2 , is calculated to be 4.63% ($=14.01/302.27 \times 100$). This value is very close to the experimental weight loss of 4.6%. Moreover, the weight loss in the temperature range of 1150-1240 K, assuming the decomposition accompanied by the evolution of O_2 composed by two oxygen atoms, is calculated to be 10.59% ($=2 \times 16.00/302.27 \times 100$). The obtained value of 10.59% may also be consistent with the experimental weight loss of 9.5% in the temperature range of 1150-1240 K. Therefore, it is probably that the weight losses below 1240 K are caused by the evolutions of N_2 and O_2 due to the thermal decomposition of PbHNSO_3 . It is seen that there is a drastic increase in weight loss above 1240 K in the TG curve. This is presumed to be caused by the evolutions of SO and SO_2 due to the thermal decomposition at high temperatures above 1240 K.

No significant endothermic and exothermic peaks in DSC curves were observed in the temperature range of 100-520 K. Generally, a clear peak in DSC and DTA curves is attributed to the change of exchange energy at phase transition. Therefore, the results of DSC and TG-DTA analysis indicate that there is no phase transition of

PbHNSO₃ in the temperature range of 100-960 K.

3.2 X-Ray Crystal Structure Description

The crystal structure of a single crystal grown from the agar-agar gel was analyzed by X-ray diffraction. The observed lattice parameters indicated that it belongs to an orthorhombic system. The systematic extinctions in the observed reflections revealed that the possible space group is *Pn2₁a* or *Pnma*. Furthermore, the intensity statistics indicated that the space group belongs to centrosymmetric *mmm* Laue class. Thus, the space group of the crystal was determined to be *Pnma*.

The atomic positions of independent Pb, N, S, and two O atoms in the unit cell were found by the direct method from X-ray diffraction data. The Pb, N, S atoms and one of the O atoms were located at special positions on a crystallographic mirror plane parallel to the *ac*-plane, and the other O atom was constrained at equivalent positions across the mirror plane. It was confirmed that a minimum *R*-value was obtained when the N atom was located at the special position determined by the direct method. The positions of remaining hydrogen atoms were not found by difference Fourier syntheses. Thus, the complete chemical formula of the crystal was not determined well in the least-squares refinement. The chemical formula built up by using the Pb, N, S, and O atoms with an electrical charge of ions was indicated by Pb²⁺NSO₃³⁻. It was found from the formula that there is one excess electron giving the negative charge of -1*e*. Therefore, it was necessary to add a hydrogen atom to the formula in order to suppress the electron concentration by one positive charge. The chemical formula of the crystal was considered to be represented as PbHNSO₃.

Table 2. Atomic coordinates and thermal parameters at 297 K with standard deviations in brackets. The anisotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) are defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^{*}c^{*}kl + 2U_{13}a^{*}c^{*}hl + 2U_{12}a^{*}b^{*}hk)]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Pb	0.31202(6)	0.25	0.33279(8)	147(2)	286(3)	199(2)	0	12(2)	0
N	0.3077(12)	0.25	0.9578(13)	89(37)	154(42)	83(33)	0	50(29)	0
S	0.4355(4)	0.25	0.8152(4)	93(10)	127(11)	104(10)	0	2(9)	0
O(1)	0.5908(12)	0.25	0.9046(16)	126(44)	308(57)	214(45)	0	-62(34)	0
O(2)	0.4165(9)	0.0271(14)	0.6914(10)	170(31)	144(27)	207(31)	-41(22)	28(24)	-11(24)

Table 3. Selected interatomic distances (in Å) and angles (in degrees) for PbHNSO₃

Distances (Å)				Angles (°)			
Pb-N ^(a)	2.607(9)	Pb-N ^(b) (2x)	3.009(5)	N ^(a) -Pb-O(1) ^(c)	133.5(3)	N ^(a) -Pb-O(2) ^(b)	67.5(2)
Pb-O(1) ^(c)	2.616(10)	Pb-O(1) ^(d) (2x)	3.267(7)	O(1) ^(c) -Pb-O(2) ^(b)	74.6(3)	O(2) ^(b) -Pb-O(2) ^(g)	69.1(3)
Pb-O(2) ^(b) (2x)	2.635(7)	Pb-O(2) ^(e) (2x)	2.748(8)	N ^(a) -Pb-O(2) ^(e)	87.2(2)	O(1) ^(c) -Pb-O(2) ^(e)	130.0(2)
Pb-O(2) (2x)	2.906(8)	S-N	1.468(10)	O(2) ^(b) -Pb-O(2) ^(e)	154.18(8)	O(2) ^(b) -Pb-O(2) ^(d)	106.4(2)
S-O(1)	1.455(11)	S-O(2)	1.487(7)	O(2) ^(e) -Pb-O(2) ^(d)	65.9(3)	O(1)-S-O(2)	110.2(4)
N-O(1)	2.426(14)	N-O(2)	2.393(10)	O(1)-S-N	112.2(6)	O(2)-S-N	108.1(4)
O(1)-O(2)	2.413(12)	O(2)-O(2) ^(f)	2.404(15)	O(2)-S-O(2) ^(f)	107.9(6)		

Symmetry codes: (a) *x*,*y*,*z*-1; (b) -*x*+1/2,-*y*,*z*-1/2; (c) *x*-1/2,*y*,*z*+3/2; (d) -*x*+1,-*y*,*z*+1; (e) -*x*+1,*y*+1/2,-*z*+1; (f) *x*,-*y*+1/2,*z*; (g) -*x*+1/2,*y*+1/2,*z*-1/2.

The positional parameters in fractions of the unit cell and the thermal parameters are listed in Table 2. The selected bond lengths (Å) and angles (degrees) are given in Table 3. Figure 2 shows perspective views of the obtained crystal structure on the *ab*- and *ac*-planes at room temperature. The observed structure of PbHNSO₃ consists of NSO₃ pseudo-tetrahedra, PbO₉N₃ polyhedra, and NSO₃-Pb-NSO₃ frameworks. The lengths of three Pb-N and nine Pb-O bonds in the PbO₉N₃ polyhedron are in the ranges of 2.607(9)-3.009(5) and 2.616(10)-3.267(7) Å, respectively. The NSO₃-Pb-NSO₃ frameworks are constructed by two neighboring NSO₃ pseudo-tetrahedra. The Pb atom lies roughly midway between the two pseudo-tetrahedra, and is bonded with

shorter Pb-N (2.607(9) Å) and Pb-O (2.616(10) Å) bonds, as shown in Figure 2. The bond length of the Pb-N bond is slightly shorter than that of the Pb-O bonds.

The lengths of one S-N and two S-O bonds in the NSO_3 pseudo-tetrahedron of PbHNSO_3 are observed to be 1.468(10), 1.455(11) and 1.487(7) Å, respectively. No significant difference in the bond length between the S-N and S-O bonds is detected. This indicates that there is no significant difference in a quality property between these bonds. On the other hand, there is an obvious difference in the correlation between the S-N and S-O bonds in the ANH_2SO_3 -type and $\text{Pb}_3(\text{OH})_2(\text{NH}_2\text{SO}_3)_4$ crystals (Belaj et al., 1987; Cox et al., 1967; Fukami et al., 2011; Manickkavachagam & Rajaram, 1984; Wadhawan & Padmanabhan, 1972; Wickleder, 2005). The length of the S-N bond in $[\text{NH}_2\text{SO}_3]^-$ anions of these crystals is significantly longer than that of the S-O bond. For example, the lengths of the S-N and two S-O bonds in KNH_2SO_3 are 1.666(6), 1.459(7) and 1.454(4) Å, respectively (Cox et al., 1967). The S-N and S-O bond lengths in $\text{Pb}_3(\text{OH})_2(\text{NH}_2\text{SO}_3)_4$ fall in the ranges of 1.614(13)-1.662(12) and 1.434(10)-1.482(9) Å, respectively (Wickleder, 2005). The difference in the bond length between the S-N and S-O bonds has been reported to be related to the difference in the properties of single and double bonds (Cox et al., 1967; Wadhawan & Padmanabhan, 1972). Thus, it is considered from the results obtained in this study that the S-N bond in PbHNSO_3 is substantially a double bond as similar to the S-O bond, and H atoms are not attached to the N atom. Because if two H atoms are bonded to the N atom, the S-N bond would be characterized by the single bond and have longer bond length, which is similar to that in the ANH_2SO_3 -type and $\text{Pb}_3(\text{OH})_2(\text{NH}_2\text{SO}_3)_4$ crystals.

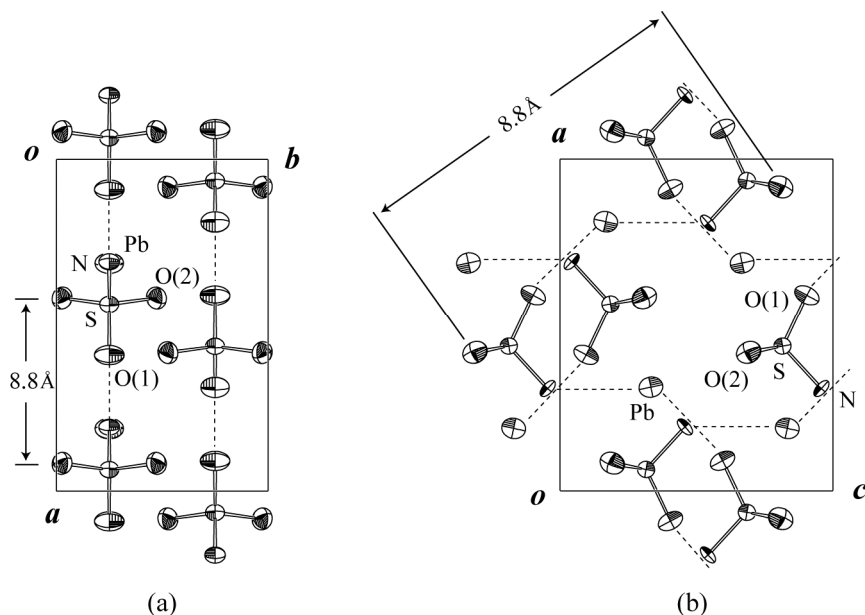


Figure 2. Projection views of PbHNSO_3 crystal structure on the (a) ab - and (b) ac -planes at 297 K with 80% probability-displacement thermal ellipsoids. The dashed lines show the Pb-N (2.607(9) Å) and Pb-O(1) (2.616(10) Å) bonds in NSO_3 -Pb- NSO_3 frameworks

Fortunately, we realized that the structure of PbHNSO_3 is very close to that of PbSO_4 (Antao, 2012; Jacobsen et al., 1998). The crystal form of PbSO_4 belongs to the same orthorhombic $Pnma$ space group, and moreover, the cell parameters, the positional parameters of all atoms, and the bond lengths are very similar to those of PbHNSO_3 . Even though there are differences in the chemical formula and crystal color. One of the two O atoms located on the mirror plane in PbSO_4 is corresponding to the N atom in PbHNSO_3 , and the PbSO_4 crystal is colorless and transparent (Antao, 2012; Jacobsen et al., 1998; Kaminskii et al., 2011). It is probably that the origin of such similar structures is due to the relatively small difference in X-ray atomic scattering factors between N and O atoms.

3.3 Crystal Color

The color of the PbHNSO_3 crystal grown by the gel method is dark brown. In general, it is well known that a unique brown color of materials is produced by the absorption of blue wavelengths of light. Thus, it is necessary for clarification of the crystal color to consider the excitation of electrons in the crystal. The energy levels E_n of

an electron in a simple potential well express as the formula, $E_n = h^2 n^2 / (8m_e L^2)$, where h is Planck's constant, n is a principal quantum number, m_e is the rest mass of electron, and L is the width of the potential well. The Pb atom is bonded to the two NSO_3 pseudo-tetrahedra, and the $\text{NSO}_3\text{-Pb-NSO}_3$ frameworks are constructed in the crystal, as shown in Figure 2. It is seen that the two NSO_3 pseudo-tetrahedra and the Pb atom in the frameworks are arranged nearly in a straight line. The distances of N-O(1), N-O(2), O(1)-O(2), and two O(2)-O(2) on the edges of the $\text{NSO}_3\text{-Pb-NSO}_3$ framework are 7.977(14), 7.939(12), 8.577(13), 8.847(10), and 9.168(10) Å, respectively. The widths of the potential well produced by the $\text{NSO}_3\text{-Pb-NSO}_3$ framework are considered to correspond to these distances. Therefore, the energies $\Delta E (=E_3-E_2)$ of the excess electrons from the ground ($n=2$) state to the first ($n=3$) excited state of the N and O atoms are calculated using the above formula with these distances. The absorption wavelengths $\lambda (=hc/\Delta E)$ in the crystal by the excitation of the electrons are calculated to be in the range of 420-550 nm. This range is very close to the wavelength range (430-500 nm) of blue and blue-green lights. Thus, it is concluded that the dark brown color of PbHNSO_3 is produced by the absorption of the wavelengths in the range of 420-550 nm in the crystal which is due to the excitation of the excess electrons.

Since the crystal structure of PbSO_4 is very close to that of PbHNSO_3 , there are $\text{SO}_4\text{-Pb-SO}_4$ frameworks of a nearly straight line in the PbSO_4 crystal (Antao, 2012; Jacobsen et al., 1998). The Pb atom is bonded to the two neighboring SO_4 tetrahedra, and the two Pb-O distances are 2.609(7) and 2.610(6) Å. Moreover, the O-O distances on the edges of the $\text{SO}_4\text{-Pb-SO}_4$ framework are in the range of 7.960(8)-9.175(6) Å. This range of the distance is very similar to that of PbHNSO_3 . Based on the above formulas and these distances, the absorption wavelengths in the crystal are calculated to be in the range of 420-560 nm. However, the PbSO_4 crystal is colorless and transparent, and does not show a dark brown color (Kaminskii et al., 2011). Thus, it is considered from these results that no excess electrons for the excitation exist in the PbSO_4 crystal, and the origin of the crystal color is caused by the presence or absence of N atoms in the crystals. The colorless and transparent characters of PbSO_4 would be produced by the absence of the N atom in the crystal, and the excess electrons in the PbHNSO_3 crystal would be stripped from the N atoms.

4. Conclusion

We have studied the synthesis, structural features, and physical properties of PbHNSO_3 . A new type of the PbHNSO_3 crystal, which is dark brown in color, is grown from the agar-agar gel by the gel method with slow diffusion. From the results of DSC and TG-DTA analyses, it is found that there is no structural phase transition of PbHNSO_3 in the temperature range of 100-1320 K, and the thermal decomposition starts at about 960 K. The crystal structure is determined to be orthorhombic with space group $Pnma$ by means of single-crystal X-ray diffraction at room temperature. It is found that the structure consists of the NSO_3 pseudo-tetrahedra, the PbO_3N_3 polyhedra, and the $\text{NSO}_3\text{-Pb-NSO}_3$ frameworks, and is very close to that of PbSO_4 . The excess electrons in the simple potential wells produced by the $\text{NSO}_3\text{-Pb-NSO}_3$ framework are possible to be stripped from the N atoms. The dark brown color of PbHNSO_3 is suggested to be caused by the absorption of blue wavelengths of light due to the excitation of the electrons in the potential wells.

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